Electrophoretic Deposition of Graphene on Copper and its Corrosion Behaviour

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In

Mechanical Engineering (Steel Technology)

By

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May 2016

CERTIFICATE

This is to certify that the work presented in this thesis entitled "**Electrophoretic deposition of graphene on copper and its corrosion behaviour**" by "**Duleshwar Singh**", Roll Number **214MM2362**, is a record of original research carried out by him under my supervision and guidance to the partial fulfilment of the requirements for the degree of "**Master of Technology**" in "**Mechanical Engineering (Steel Technology)**". Neither this thesis nor any part of it has been submitted for any diploma or degree to any institute or university in India or abroad.

Prof. Archana Mallik
Supervisor

DECLARATION

I, **Duleshwar Singh**, Roll Number **214MM2362** hereby declare that this thesis entitled "**Electrophoretic deposition of graphene on copper and its corrosion behaviour"** represents my original work carried out as a postgraduate student of NIT Rourkela and, to the best of my knowledge, it contains no material previously published or written by another person, nor any material presented for the award of any other degree or diploma of NIT Rourkela or any other institution. Any contribution made to this research by others, with whom I have worked at NIT Rourkela or elsewhere, is explicitly acknowledged in the thesis. I have also submitted my original research records to the scrutiny committee for evaluation of my thesis.

I am fully aware that in case of any non-compliance detected in future, the Senate of NIT Rourkela may withdraw the degree awarded to me on the basis of the present thesis.

May, 2016 **Duleshwar Singh**

NIT Rourkela

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Duleshwar Singh

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ABSTRACT

Graphene is a single layer of pure carbon atom that are bonded together in hexagonal or honeycomb lattice structure. The gradual destruction of metal surface by chemical or electrochemical reaction with their environment forms corrosion. The graphene layer has been used as protective thin film on metal surface by electorphoretic depositon (EPD). In the present work, graphene has been synthesized by electrochemical intercalation and exfoliation of pyrolytic graphite sheet by various electrolytes (H_2SO_4, HNO_3, and $HCLO_4$) in varying concentration. The prepared dispersed graphene oxide (GO) solutions were deposited on copper surface with working area of $2cm^2$ by electrophoretic deposition technique at various (0.1, 0.5, 1 wt %) concentration of graphene. The sodium dodecyl sulfate (SDS) anionic surfactant has been used as binder to increase the thickness of coating. The graphene oxide coatings were used with the aim that it will act as a protective layer for corrosion of Cu substrate. The thickness of the graphene coated thin film was characterized by surface profiler and atomic force microscopy. Morphology of graphene nano sheets and coated graphene was analyzed by FESEM, which has showed clearly microstructure of GNS layer. Topography of graphene coated specimen characterized by AFM and crystal structure, crystalline planes and phases of graphene sheet were characterized by X-ray diffraction. (0 0 2) and (1 0 0) planes showed the graphene sheet has been confirmed by X-ray diffraction. The electrochemical corrosion behavior of graphene coating on Cu in 0.1M NaCl solution has been investigated by potentiodynamic linear sweep voltametry technique. However, the tendency (corrosion potential) is nobler for bare copper substrate. The study needs further experiment and optimization to reach to an affirmative conclusion. The application of GO layer has improved the corrosion resistance property of coated Cu due to better barrier quality of GO layer.

Keywords: Graphene, electrochemical exfoliation, electrophoretic deposition, linear sweep voltammeter, X-ray diffraction,

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Chapter 01

Introduction

1. Introduction

Graphene is discovered in 2004, by Geim and Novoselov [1]. They rinsed thin layer of graphite by mechanical exfoliation and produced graphene. It is the thinnest layer of carbon atom and strongest material in the world [2]. Graphene can be defined as the single layer of graphite or carbon atom, which is bonded in 2-dimensional hexagonal or honeycomb lattice structure. It has distinct properties, compared other like as high electrical conductivity, high mechanical strength, high thermal conductivity, super hydrophilic properties etc. Due to unexcelled properties of graphene can be used in various technologies such as composite material, graphene based electronic, molecular gas sensor, batteries, transistor and biosensor. Graphene have been synthesize in various methods such as chemical vapor deposition, hummer's method, epitaxial growth of graphene on SiC and micromechanical cleavage can obtained only limited amount of graphene [3].

Synthesis of graphene by electrochemical technique has implemented in recent year. It is simple, fast and eco-friendly capable of produces high quality graphene thin film but lower yield. They have produced large sheet of graphene comparatively other [4]. Many researchers have used graphene as a protective layer on metal to prevent from corrosion. The graphene deposition on conductive substrate different method has been reported such as thermal decomposition and electrophoretic deposition (EPD) [5]. EPD process is a low cost, non toxic and performed at ambient temperature and pressure. Colloidal deposition methods include EPD which can be used to deposit nano-sized functional materials on a conductive substrate. Recently, EPD has been attracting more attention for the deposition of nano-particles, thin layer films on solid conductive substrate. It is cost effective and can be used for a various application [6]. In this project work, EPD was used to deposit graphene layer on copper and corrosion behavior of graphene coated

layer has been investigating. Copper is the most widely used materials due to its excellent thermal and electrical conductivity [7]. Oxidation of copper is serious problem in microelectronic, nano electronic, sensor, transistor and other application. Development of simple, long lasting and efficient anticorrosion protective layer that provides requisite protection of surface from oxidation and corrosion is most warranted for its use in above applications. However, many of these techniques have some inherent problems, such as higher thickness of the coating, shift in optical properties, deterioration of thermal and electrical conductivity of copper, poor adhesion, etc [8].

1.1. Motivation

Electrophoretic deposition technique is simple, fast and cost effective than others. Graphene thin film is used as corrosion protective layer because it has super hydrophobic and hydrophilic properties. The objective of this project obtained corrosion resistive graphene thin layer to protect the Cu substrate. The optimization studies were carried out at various concentrations and along with sodium dodecyl sulfate (SDS) as an extra additive.

1.2. Objectives of present work

This project effort is electrophoretic deposition of graphene on Cu and the study of corrosion behavior in different concentration of graphene coated substrate. Corrosion test perform in chloride solution with same parameters.

The purpose of this project work is as follows:

- Synthesis of graphene by electrochemical exfoliation technique.
- Thin layer of graphene obtained on Cu surface by electrophoretic deposition.
- Characterization of electrophoretic deposition layer by XRD, FESEM, AFM and surface profiler.

- To study electrochemical corrosion behavior of graphene deposited thin film on Cu by potentiostat.

1.3. Outline of thesis

The project work carried out with synthesis of graphene, electrophoretic deposition of graphene and study of its corrosion behavior.

The chapter 2 covers the literature on graphene and its properties, different technique of graphene synthesis and electrochemical synthesis, electrophoretic deposition and corrosion studies.

The chapter 3, gives details of experimental method of graphene preparation, coating by electrophoretic deposition, characterization of graphene thin film by X-ray diffraction, field emission scanning electron microscope, surface profiler, atomic force microscope and corrosion study by potentiostat using linear sweep voltammeter.

The chapter 4, results have been discussed graphene intercalation and exfoliation result in linear sweep voltametry, crystal structure and planes has analyzed by X-ray diffraction, and morphology analysis result carried out in FESEM, topography analysis and thickness of thin film of graphene has been analyzed by AFM and surface profiler, corrosion behavior results have been illustrated in this chapter.

In chapter 5, results details have been illustrated and conclusive remark were included.

Chapter 02
Literature Survey

This chapter covers the literature on graphene and its properties, different technique of graphene synthesis, electrochemical synthesis, electrophoretic deposition and corrosion studies

2. Literature survey

2.1 Graphene

In recent year graphene, is a single layer of pure carbon atoms that are bonded together in hexagonal honeycomb lattice structure [9]. It is two-dimensional crystalline allotrope of carbon and has been investigated because of their distinct properties such as chemical stability, large surface area, high current density, ballistic transport, super hydrophobic at nanometer scale, electrical properties, optical properties, and mechanical properties. The initial work of the isolation of carbon thin film and monolayer graphene using scotch tape method showed by Geim and Novoselvo.The graphene was extracted first time using a method called mechanical exfoliation from bulk graphite. This method assent easy production of high quality graphene crystallites and further led to enormous experimental activities [10]. In this strategy, a bit of tape is utilized to peel graphene pieces off lump graphite which is basically a pile of graphene sheets. This method is still used in many laboratories to obtain graphene layer and to prepare proof of concept devices.

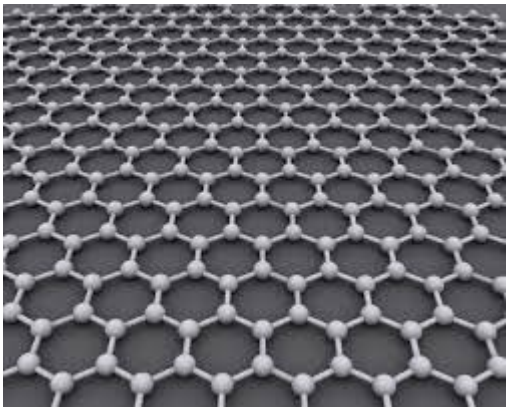

Figure 1: Single layer of graphite sheet (Graphene)

2.2 Properties of graphene

The graphene hexagonal lattice is composed into two equivalent sub lattices of carbon atoms bonded together with σ bonds. Graphene has specific properties from other materials such as,

2.2.1 Mechanical properties

The mechanical properties of monolayer graphene have high Young's modulus and breaking strength. Graphene got the title of "strongest material ever" through the confirmation of its sustaining Young's modulus of 1 TPA and breaking strength of 125 GPA with an intrinsic mechanical strain of 25%. Numerical simulation and semi empirical model have successfully estimated the Young's modulus and other mechanical quantity of graphene [11]. Graphene has high fracture strength and as the strongest material ever measured, some 200 time stronger than structural steel.

2.2.2 Electronic properties

An electronic property is the most useful property of graphene is that it is a zero band gap semiconductor, with high electrical conductivity. Graphene shows a bipolar electric field effect and charge carriers can be turned between electrons and holes. Electron mobility of graphene is high and lowest resistivity substance at room temperature, these electron are called π electrons and are located at above and below the graphene sheet. Moreover the watched mobility depend feebly on temperature, recommending that an ultrahigh mobility could be realized in graphene at room temperature.

2.2.3 Optical properties

A single layer of graphene is able to absorb spectrum as high as 2.3% of white light. It has a unique and interesting property, especially when considering single layer of graphene. Monolayer of graphene increases the amount of white light absorb by approximately the value 2.3%.

2.2.4 Thermal properties

Thermal conductivity of graphene is about 5000 W/mK at room temperature predicted for a suspended monolayer graphene, this value much higher than that of graphitic carbon. Conductivity of graphene is almost highest than any material, and heat transfer rate is high due to its thermal property.

2.3 Synthesis of graphene

Synthesis of graphene was tried in 1975, showed the fabrication of single and multi layer graphite by thermal decomposition of carbon on single crystal platinum substrates [12]. The process was not studied extensively at that time due to lack of consistency between properties of such sheets. Nowadays, different techniques have been established for synthesis of graphene is detailed below.

2.3.1 Mechanical exfoliation

Mechanical exfoliation is the first method of graphene synthesis. This is a top-down technique by which a longitudinal or transverse stress generated on the layer of a substrate material, a piece of scotch tape or AFM tip using the single layered structure is generated on the surface of the material. Several layers of graphene stacked from graphite sheet, is bonded together week by Van der Waals force. Thus in principle, graphene is possible to produce a high purity graphite sheet, if these bonds can be broken. Exfoliation and crack use mechanical or chemical energy to break bonds in the week and individual graphene sheets separate. First attempt in this direction was made by Viculis et al., who have used potassium for a pure graphite sheet metal intercalate and exfoliate carbon sheet with ethanol as the dispersion [13]. The mechanical exfoliation process shows good promise to synthesize large scale graphene and some of the recent modification, through liquid phase exfoliation, possible to produce large size graphene.

2.3.2 Hummers method

Hummers method is producing graphene by oxidizing graphite to graphite oxide (GO) by using strong oxidizing agent such as $KMnO_4$ and $NaNO_3$. On oxidation, increase the interlayer spacing by reducing the interlayer Van der Waals forces. This method introduces the way to get more stable GO solution. The GO colloidal solution then exfoliated into graphene with single to multilayer by heating or ultra-sonication. The single layer graphene prepared has a high function groups and reduction need to be obtained graphene like properties. Chemical reduction has been achieved by addition of some certain reducing agent such as hydrazine to give well dispersed single layer graphene sheets [14]. Thermal reduction and exfoliation of graphite oxide also produce good quality graphene.

2.3.3 Chemical vapor deposition

Chemical vapor deposition is a process carried out at high temperature range between 800-1000°C. It is the most promising, cheaper and readily available approach for the deposition of high quality graphene is CVD onto transition metal substrate such as Ni and Cu. CVD process in which use gaseous reactant to deposit on a substrate. The process is based on carbon saturation upon exposure to a hydrocarbon gas at high temperature of a transition metal. The solubility of carbon in the transition metal decrease when cooling the substrate and from the surface thin film of carbon is thought to precipitate [15].

2.3.4 Epitaxial growth of graphene on SiC

Epitaxial growth of graphene is a process to form high crystalline graphene onto surface of SiC substrate. It is one of the most popular methods of graphene synthesis and has been discovered vigorously for the last few years. The deposition of thin film of graphite or graphene on SiC surface is known as hetero-epitaxial layer. The growth of graphene is its large area growth on SiC surface by evaporation of Si and prepares thin film graphene with carrier mobility. This method is carried out at high temperature (1000°C-1500°C) and an ultrahigh vacuum or atmospheric pressure [16].

2.3.5 Electrochemical Exfoliation

Electrochemical exfoliation process is a simple, cheaper, fast and environment friendly synthesis of graphene. It is a new one step method to produce high quality few layer graphene sheets and operates at atmospheric pressure and temperature. In this method electrochemical exfoliation of graphite is carried out in electrolyte, where graphite using as anode (working electrode) and platinum or graphite rod as cathode (counter electrode). Electrochemical setup in which first working electrode connect at cathode for producing intercalate surface, after then connect into the anode. Exfoliation of graphite occurs at anode and produces few layer graphene or graphite oxide (GO) due to ion present in the electrolyte or it depends on the nature of electrolyte. The intercalating ions in the solution penetrate into the graphite sheet due to applied potential. During the exfoliation two types of graphite flakes form, one is thick layer they are settling down

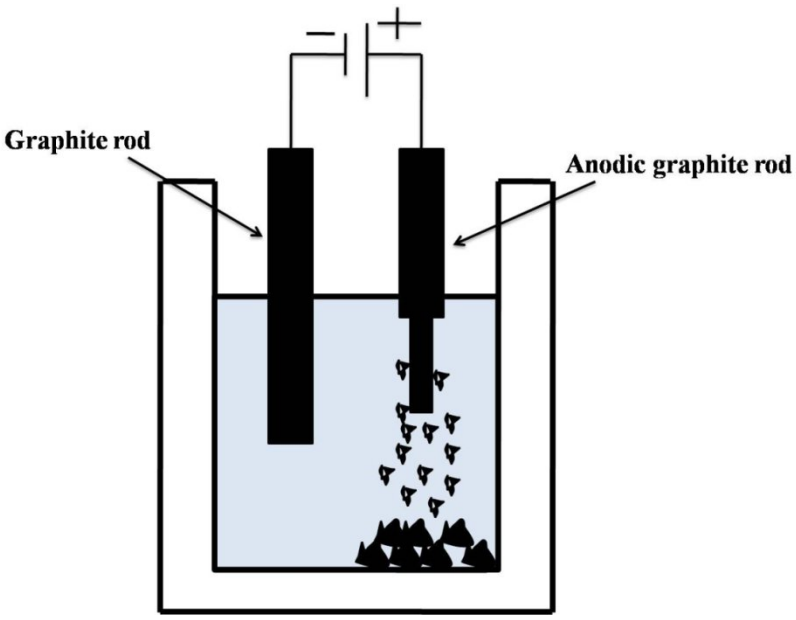

Figure 2: Schematic diagram of the electrochemical synthesis of graphene process

bottom and other formed of layer float on the surface of solution. The graphene oxide solution wash with distilled water and ultra-sonication perform for complete dispersion of GO suspension. Some stabilizer can also use in the solution for stabilization long period of time, then finally in this process solution is taking for centrifugation to separate the particles form of graphite from the graphene or GO solution and the solution either dried or can take directly for characterization.

Electrochemical exfoliation has many advantages over other technique.

- Thin layer of graphene film can be obtained.
- The process is high yield and easy to operate.
- This technique is very fast, simple and environment friendly over other process.
- Graphene produces functionalize group depend on the electrolyte nature.

2.4 Electrophoretic deposition

The electrophoretic deposition is a method with a wide area of application in the processing of coating and ceramic material. The EPD is one of the ceramic production processes in colloidal. It is very versatile process so it can be easily modified for a special application. Electrophoretic deposition can be done on any shaped sample such as plane, cylindrical or circular with minor changes of design and position of electrode. In the EPD process deposited film thickness and surface structure can easily controlled by adjustment of applied voltage and coating time [17]. Eletrophoretic deposition is a particulate forming process. It begins with dispersed powder material in a solvent and uses an electric field to move the powder particles into a desired arrangement on an electrode surface. It is simple, cheaply technique to deposit thin film on electrode surface by applying electrical parameter voltage or current.

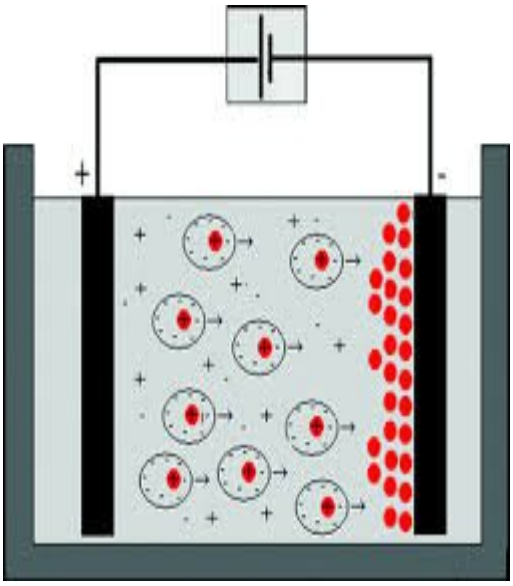

Figure 3: Schematic diagram of electophoretic deposition

In this process two or three electrode system is using, in which anode as counter electrode and cathode as working electrode. By applying D.C. (Direct Current) between the anode and cathode, when the particles are positively charged then the deposition occurs at cathode and negatively charged particles a deposit at anode. The electrophoretic deposition setup consists of following:

- Electrolyte
- Anode
- Cathode

Advantages of electrophoretic deposition over other deposition techniques:

- Deposition is carried out at room temperature and easy to operate.
- Complex fabricated object can be easily deposited.
- The coating composition easily controlled.
- Applicable to wide range of materials and greener (no toxic) gas or chemical formed compare to other technique.

2.5 Corrosion studies

Corrosion is defined as the degradation or deterioration of metal surface due to chemical or electrochemical reaction between it and the surrounding environment. The atoms are present in nature in chemical compounds. The energy required to extract the metal are same as the minerals are emitted when react chemical reaction with the surrounding. Corrosion returns to the metal in chemical compounds that are equal or similar to the minerals form, from which metal was extracted. Thus corrosion is known as extractive metallurgy in reverse [18]. Corrosion is a broad term we have observed many types of corrosion in our daily life, such as rusting of iron, leakage of pipe, some time in bicycle parts corroded during rainy season and metals contact in environment getting corroded. Many dollars spent every year in industries and other sector due to corrosion. In this time many research and development has done to develop the corrosion resistance property metals by various method or technique. Corrosion is a big global problem for every metallic metals. Copper is the one of most important materials used in marine engineering, industry, power station, heat exchanger, pipelines, heat conductor because it has high thermal and electrical conductivity, mechanical workability. Thus, the corrosion of copper and increasing corrosion resistance property of metal in wide variety of media attracted. Copper can be corroding in marine engineering due to high amounts of chloride ions present [19]. Copper has good corrosion resistance and behaves like a noble metal, when the copper change to reddish brown is destroyed and not repairable, which means copper will corrode.

Figure 4: Showing the corrosion on copper pipe

A common method used to protect the metal surface by conductive polymers coating on surfaces. These coating forms corrosion barrier between the metal surface and the surrounding environment but effectively when coating covers all structure. In coating technology increasing the development of an effective corrosion coating that can replace the inorganic anti-corrosion such as paints, which may have harmful impact on health and environment.

Chapter 03
Materials and methods

This chapter gives details of experimental method of graphene preparation, coating by electrophoretic deposition, characterization of graphene thin film by X-ray diffraction, field emission scanning electron microscope, surface profiler, atomic force microscope and corrosion study by potentiostat using linear sweep voltammeter

3. Materials and Methods

3.1 Graphene preparation

All the chemical, material and solvents used were of analytical grade and have been used without further purification. Highly pyrolytic graphite sheet with the thickness 3 mm was employed as both the working as well as counter electrode in a voltage regulated DC bias system (Aplab, Model No. 7103). All experiments were operated at ambient condition of temperature and pressure. Graphene has been prepared by electrochemical exfoliation, where graphene is detached from an already existing graphite sheet. In a typical electrochemical exfoliation of graphene, a conventional two electrode system was used, which consisted of two graphite electrode flakes as anode and cathode. Highly pure pyrolytic graphite of 1.0cm x 1.5cm x 0.3cm were taken as working electrode for exfoliation reaction in aqueous solution H_2SO_4, HNO_3, and $HCLO_4$ at 1.5 molar concentration. In the synthesis process, a fresh graphite sheet was used as a working electrode (WE) by blanketing the remaining portion by adhesive tape. The counter electrode was also the same graphite sheet but more contact area with the electrolyte. The process of exfoliation, working electrode (WE) was given a cathodic pre-treatment 3V for 10-15 min to absorb physical impurities and produce surface of graphite sheet more efficient for intercalation. After then the pre-treated graphite electrode used as the anode in the electrolytic bath with a successive increase of applied voltage 0 to 8V and voltage when reached up to 8V, the electrolyte bath was given a stagnant voltage for acute exfoliation. The graphite sheet exfoliated out as black product was collected at the bottom of the bath. The product was thoroughly washed by distilled water and remove acidic content from the exfoliated graphite flakes. The exfoliated flakes were taken for ultra-sonication 4 hours to disintegrate the graphite flakes [20]. After sonication sample was taken in centrifuge tube at same weight, now homogeneously dispersed graphene colloidal is centrifuged at 5500 rpm for 30 min. For further characterization of sample, either it was oven dried after filtration or dispersed.

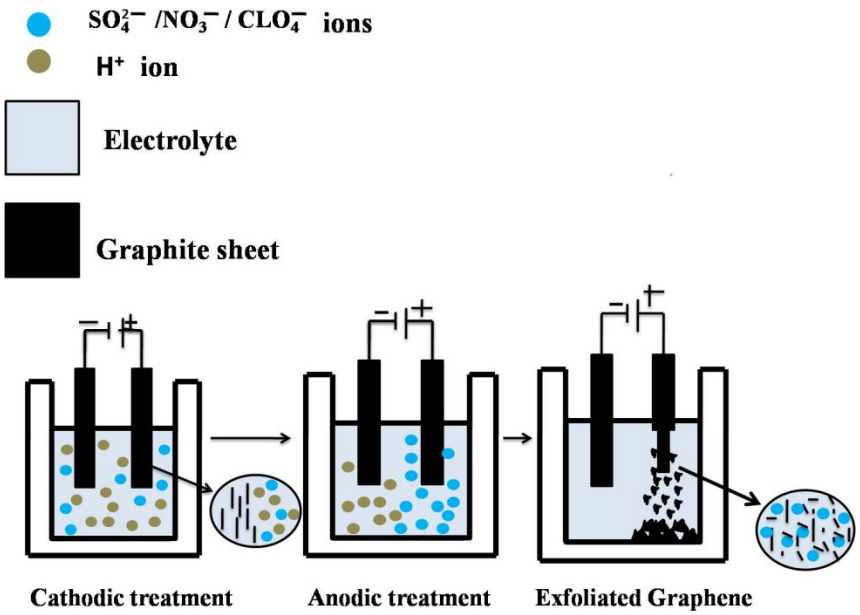

Figure 5: Schematic diagram of graphene preparation by electrochemical synthesis process

Then, the graphene nanosheets (GNS) were taken from oven after heating and prepared solution for electrophoretic deposition (EPD). Different concentration of graphene oxide (GO) were prepared for EPD process such as 0.1 wt %, 0.5 wt% and 1 wt%.

3.2 Electrophoretic deposition

Electrophoretic deposition of graphene oxide was carried out onto copper substrate with working area of 2 cm^2. The EPD setup has consisted of two parallel copper plates, in which one was used as working electrode and another as counter electrode. The working distance between working and counter electrode was 10 mm and connected to a D.C. voltage using system (Aplab, Model No.7103). Anode and cathode were used as working and counter electrode. First in EPD process GO solution was sonicated for 2 min and the copper plates cleaned through etchant such as diluted hydrofluoric acid and acetone. The sodium dodecyl sulfate (SDS) anionic surfactant was used as binder in graphene oxide solution. When voltage applied 15 V onto the suspension GO particles deposited at the anode with deposition time was 15 min. The EPD was performed at different concentration with fixed voltage and time [21]. The coated sample were instantly dried by dryer and then dried at room temperature.

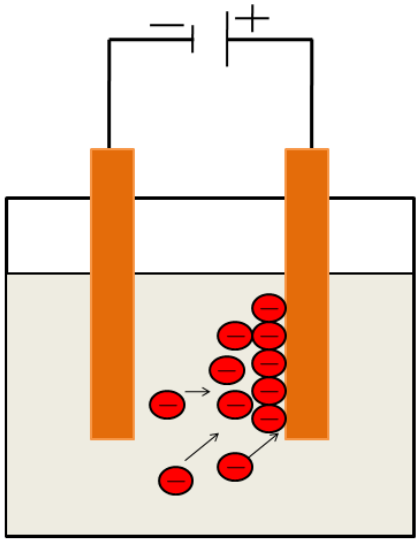

Figure 6: Schematic diagram of EPD coating of GO particle on Cu

3.3 Characterization

Synthesized few layer of graphene nanosheets (FLGNSs) and coated thin film of graphene on copper has been characterized by using various precision scientific instruments. X-Ray diffractions (XRD) technique has been used to investigate the structural planes, phases and d-spacing of FLGNSs and thin film of graphene. Surface profiler used to measure the thickness of coated thin film of graphene on copper substrate. To investigate the morphology analysis of FLGNSs and coated thin film of graphene has been done by using field emission scanning electron microscope (FESEM). Topography analysis of coated thin film of graphene has been carried out by phosphorous doped silicon probe in contact mode atomic force microscope (AFM).

3.3.1 X-Ray diffraction

X-Ray diffraction analysis has been done for few layer graphene nanosheets (FLGNS) in the range of 2θ from 5° to 70° at the scan rate 10°/min with the time step 0.02 at CuKα radiation (λ= 0.154 nm) using Rigaku Model: Ultima IV. X-ray diffraction technique is based on Bragg's law,

which is used to determine crystal structure, phases and orientation of planes. It can also provide information about unit cell dimension of crystalline material. The principle of X-ray diffraction based on constructive interference between monochromatic X-ray and crystalline material. This X-rays beam generated from cathode tube, to yield radiation and emits to the sample or material produces diffracted rays by Bragg's law.

3.3.2 Field emission scanning electron microscope

Surface morphology analysis has been done by FESEM Model: Nova NanoSEM 450. Field emission scanning electron microscope is an analytical technique used to study the microstructure of material and their electronic properties. A FESEM examination of the electron gun in cathode narrower offers on the lower level as well as high energy electron beams, the spatial resolution improved, resulting in charging and minimal sample harm. The imaging technique is used for applications, which demand the highest possible magnification.

3.3.3 Atomic force microscopy

Topography analysis of graphene coated thin film has been done by silicon nitride probe in contact mode using lab programmed Vecco di Innova, atomic force microscopy. The AFM has consists of cantilever sharp silicon probe at the end and the tip used to scan the surface of specimen. When the silicon probe brings in to the surface of specimen, forces between silicon probe and specimen lead the deflection according to Hooke's law. Different types of forces can measured by AFM depending on situation such as Van der Waal force, mechanical contact force, magnetic force, chemical bonding, electrostatic force etc. When the tip is in contact mode, it dragged across the specimen surface and the profile of the surface are measured either using directly deflection of cantilever or keep the cantilever at a constant position. AFM has various advantages over other techniques:

- AFM gives 3-D surface profile and high resolution.
- In AFM not required any treatment such as metal or carbon coating.
- Atomic force microscopy can works in atmospheric temperature or environment.

3.3.4 Surface profiler

Surface profilometer has been carried out in Veeco dektak 150. The surface thickness of coated sample and height difference was measured by profiler. This instrument runs by the stylus making contact between surfaces of sample and moving front to back for measuring the height difference of surface. Part of the investigation of the device tool is located with a dark plastic case on segregation platform to inhibit disintegration in measurement by atmospheric condition and acoustic noise. By opening the door on the front of the unit tool is accessed. The features and specification of dektak 150:

- Scan direction front to back.
- Stress measurement and three dimension scan.
- Stylus radius 2.5 μm.

3.4 Potentiostat corrosion test

Potentiostat corrosion test has been performed by using linear sweep voltammetry. It is a technique, in which potential applied between the working electrode and a reference electrode swept linearly in time while the current measured at working electrode. The experimental setup is consists of three electrode and utilize a patentiostat to deliver the potential to an electrolyte. All the electrochemical measurement has been performed in 0.1 M NaCl electrolyte in three electrode setup of potentiostat using a gamry reference 600 TM, where the working electrode graphene coated Cu substrate with the working area of 2 cm^2 was stabilized in 0.1 M NaCl solution at ambient condition. The platinum rod was used as counter electrode with high surface area compared to working electrode, saturated calomel electrode was used as reference electrode. The graphene coated sample was polarized from -1.1V to 0 V at the scan rate of 5mV/s. When increase the potential at the working electrode oxidation occurs due to molecules move from working surface and new molecules contact with working electrode [22].

Chapter 04
Results and discussions

Results have been discussed in this chapter, graphene intercalation and exfoliation result in linear sweep voltametry, crystal structure and planes has analyzed by X-ray diffraction, and morphology analysis result carried out in FESEM, topography analysis and thickness of thin film of graphene has been analyzed by AFM and surface profiler, corrosion behavior results have been illustrated in this chapter

4. Result and \discussion

4.1 Exfoliation of graphene in linear sweep voltametry

Electrochemical exfoliation of graphite sheet has been done in different electrolyte H_2SO_4, HNO_3, and $HCLO_4$ at 1.5M concentration. In the sequence working electrode connected to the cathode for 3V. The exfoliation occurs when WE connect to anode at the voltage range of 0 V to 8 V. The synthetic grade of graphite electrode has used, it consist of lamellar graphitic crystal and stacked in 3- dimensional structure. Due to Van der Waal force lamellar graphite is layered into double bonded hexagonal carbon. Therefore, intercalation size should be improved sufficient to enter in hexagonal carbon layer. The production of FLGNS during exfoliation followed by two reactions:

Cathodic reaction: In this reaction graphite sheet connected at cathode applying voltage 3V for 15 min, the graphite crystal absorbed H^+ ions from electrolyte and released vigorously hydrogen gas at cathode. Therefore, surface impurity of graphite lattice removed and produced more intercalated surface.

$$C_{\text{lattice}} + H^+ \rightarrow C_{\text{lattice}} H_{\text{absorbed}}$$

$$C_{\text{lattice}} H_{\text{absorbed}} + H_2O + e^- \rightarrow C_{\text{lattice}} (\text{expanded}) + H_2\uparrow + OH$$

Anodic reaction: In this reaction graphite electrode connected at anode and applied voltage 0V to 8V with voltage step of 0.5 V increasing with time in an aqueous different solution. At low voltage range small bubbles and gases formed. The pretreated efficient intercalated electrode surface produced oxidation and carboxylation of exfoliated graphite compound.

$$C_{\text{lattice}} (\text{expanded}) + \text{Anions} + H_2O \rightarrow C_{\text{lattice}} (\text{exfoliated}) \text{ Anions} + CO_2 + O_2$$

Due to electrochemical reaction at anode CO_2 and O_2 gases released and multilayer exfoliated graphite flakes settle down at the bottom [23]. However, thin graphite flakes consist of graphene nano sheet has found in bulk electrolyte.

The electrochemical exfoliation of graphene has carried out in the different electrolyte H_2SO_4, HNO_3, and $HCLO_4$ are stated as S_3, N_3, and C3 respectively. Figure 4.1 shows the relation

between voltage and current change with respect to time for different electrolyte. The graph between voltage and current shows initially increase the current up to exfoliation point and decreases current during expansion or exfoliation of graphite flakes. In the H_2SO_4 electrolyte (S_3), the intercalation and exfoliation of graphite flakes is high and produces higher current average causing very small particles of graphite flake exfoliated out from working electrode. The exfoliated electrolyte is not transparent due to homogeneous distribution of graphite flakes. The higher current average indicates that generation of new layer of graphite lattice is very fast and generated thin layer of graphite flakes. Current exponentially decreases about 2700 sec because thinning graphite flakes. In HNO_3 electrolyte (N_3), the intercalation and exfoliation of graphite flakes slow as compared to sulfuric acid electrolyte. During anodic reaction small graphite flakes exfoliated from the electrode and semi transparent electrolyte produced.

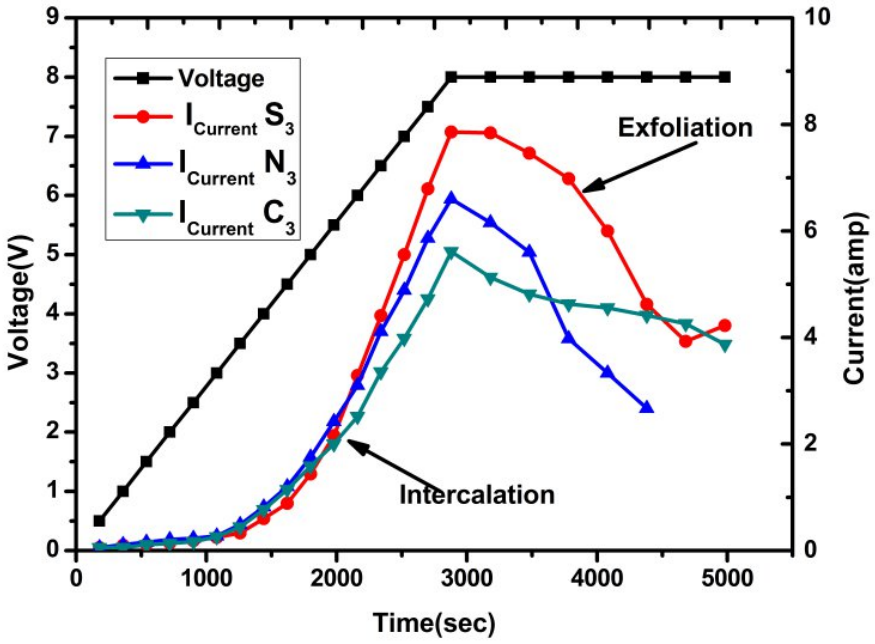

Figure 7: Relation between current, voltage and time during electrochemical exfoliation

In HNO_3 electrolyte (N_3), the intercalation and exfoliation of graphite flakes is slow as compared to sulfuric acid electrolyte. During anodic reaction small graphite flakes exfoliated from the

electrode and semi transparent electrolyte produced. Hence, thick layer of graphite flake produced in electrolyte. In $HCLO_4$ electrolyte (C_3), the exfoliation of graphite flakes is very slow, that has showed in the exfoliation graph. The intercalation of graphite flakes in C_3 electrolyte initially the current increases slowly and at around 5V it starts exfoliation. The localized stress in graphite lattice more prominent, thus results in thick layer of graphite settle down at the bottom electrolyte. In case of $HCLO_4$ exfoliation layer by layer exfoliation occurs at anode and solution after exfoliation is transparent because of heavy size of graphite flakes exfoliated. The start of full exfoliation at I_{max} (S_3) = 7.0 amp, I_{max} (N_3) = 5.8 amp and I_{max} (C_3) = 5.0 amp respectively and current decreases with detached number of graphite layer.

4.2 XRD analysis

XRD analysis has been carried out the exfoliated graphene nanosheets at 1.5 M H_2SO_4, HNO_3, and $HCLO_4$ electrolyte condition to investigate the crystalline planes and d- spacing of materials. The exfoliated graphene nanosheets in XRD pattern shows intensive peak 30.73°, 30.81°, and 30.92° (2θ values) for S_3, N_3, and C_3 graphene nanosheets.

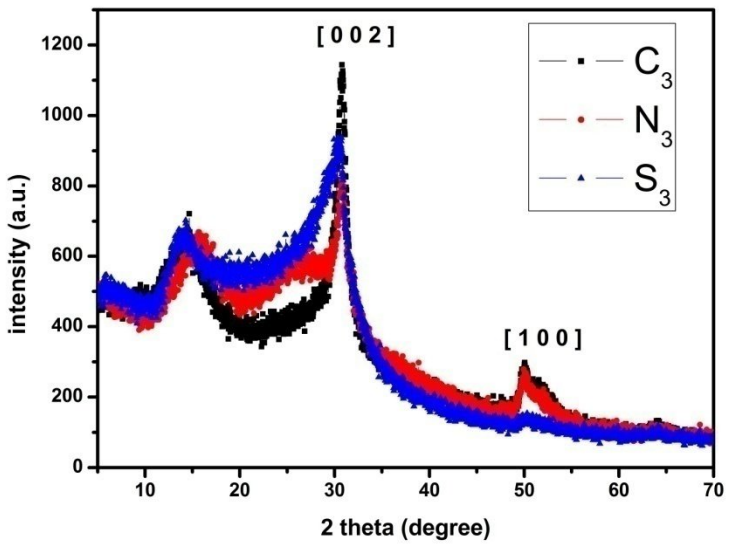

Figure 8: XRD pattern of graphene nanosheets exfoliated at different electrolyte S_3, N_3 & C_3

The corresponding to peak, d-spacing values are 0.337, 0.336, and 0.335nm. The peak shows (0 0 2) and (1 0 0) crystalline planes. The value of d-spacing of S_3 graphene sheet higher than other, and the plane (0 0 2) shifted to lower angle 30.92 to 30.73°. The increase in d-spacing of graphene sheet with increase interlayer spacing of graphite lattice, results in the intercalation and exfoliation rate is higher [24].

4.3 FESEM analysis

The morphology analysis of EPD layer of graphene on Cu has been done by FESEM. Microstructure of EPD graphene film on Cu substrate, deposited at different EPD solutions. The micrograph S_3 and N_3 graphene coating show some portion was uniform and they have contained micro cracks, crust and wafer. The microstructure C_3 shows thick layer of EPD film [25].

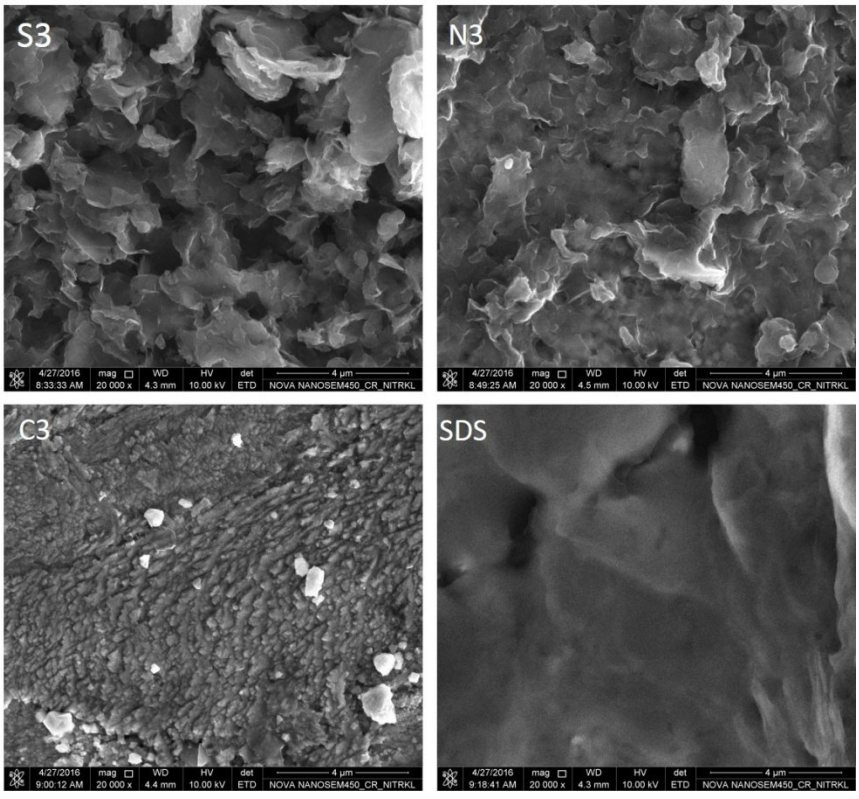

Figure 9: FESEM image of graphene film on Cu substrate, with various EPD solutions

EPD layer with SDS solution, the microstructure shows homogeneous or uniform graphene layer in same magnification. Figure 10 (a) shows, GO deposited on Cu and some parts are non-coated. Fig 10 (b) showed uniformed GO on the substrate and small dark portion are porous.

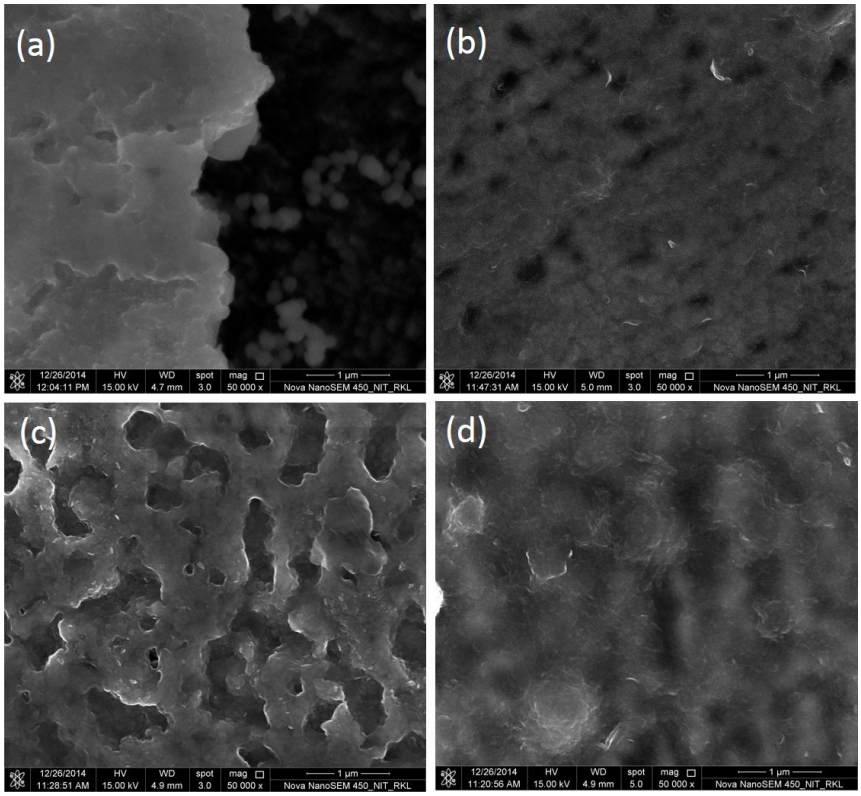

Figure 10: FESEM image of (a) Coated and non coated Cu, (b) EPD GO on Cu, (C) Coating at low concentration, (d) Coating at high concentration

In Fig (c) EPD GO layer by layer structure show because coating has done in low concentration. At high concentration Fig (d) microstructure of EPD layer uniform and thickness of layer is more. The entire images are in same magnification.

4.4 Surface profiler analysis

Surface thickness of electrophoretic deposited graphene has been determined by surface profiler. The nitric graphene oxide N_3 (GO) deposition on Cu has high thickness layer (1.5µm >0.68 µm >0.54 µm) compared to sulfuric S_3 and perchloric C_3 GO coating.

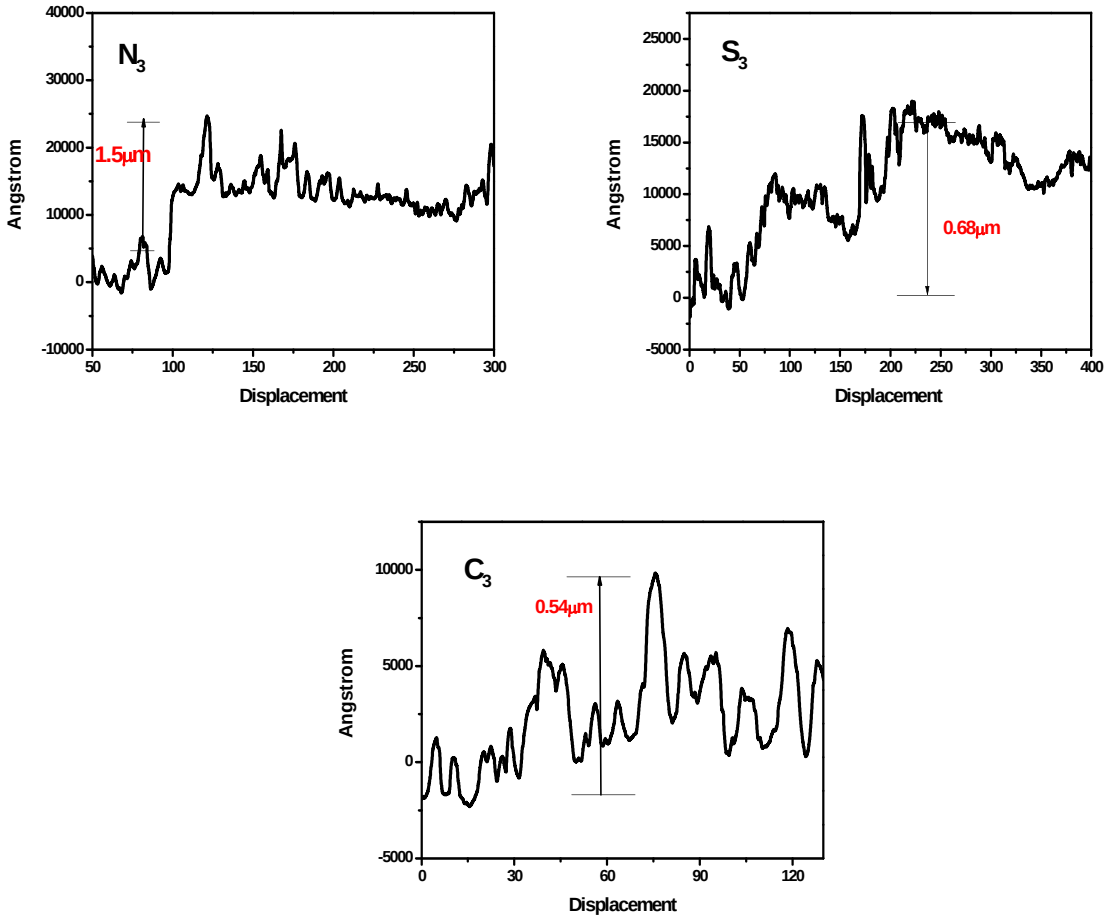

Figure 11: Graph of thickness of graphene coated Cu from surface profiler

4.5 Corrosion behavior

Corrosion behavior of graphene coated thin film on copper has been carried out in potentiodynamic using linear sweep voltametry in 0.1 M NaCl solution. The oxidation occurs on copper in chloride solution because chloride ions very corrosive for Cu when contact with its environment [26]. When the potential applied on graphene coated Cu in electrochemical cell current got between counter electrode and oxidation occurs at coated surface. After the nose point of corrosion potential oxide layer forms on the surface and which prevent further oxidation. The potentiodynamic curves of graphene coated Cu shows corrosion potential (V_{corro}) more negative value (-349.7, -329.6) from table.1 compared to bare Cu (-264.1) resulting that corrosion resistance of coated Cu lower than bare Cu.

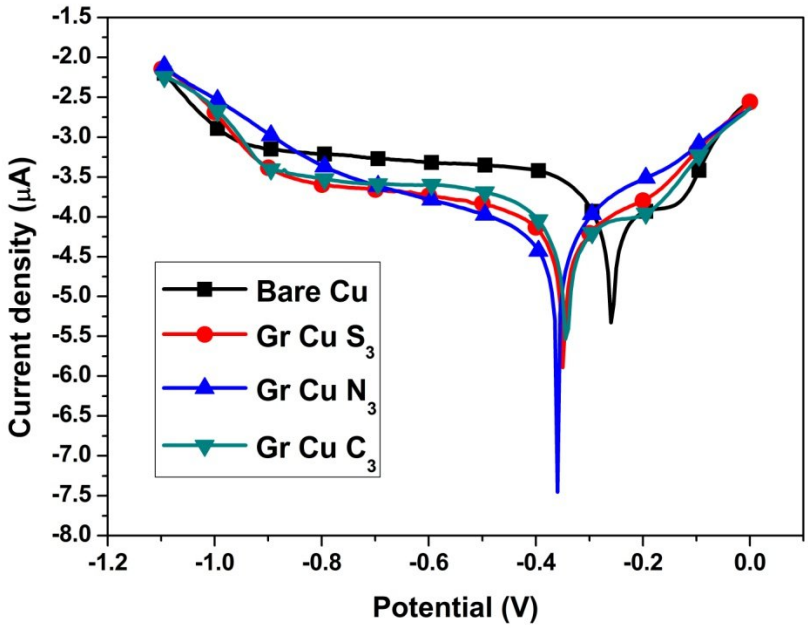

Figure 12: Potentiodynamic curve of bare Cu and 0.1 wt % concentrations EPD graphene coated Cu

Table 1: Corrosion results of 0.1, 0.5 &1 wt % concentration coated sample in 0.1 M NaCl solutions

Deposition Condition		V_{corro} (mV)	I_{corro} (µA)
	Bare Cu	-264.1	5.56
0.1 wt % Concentration	C_3	-349.7	2.90
	N_3	-364.8	0.035
	S_3	-349.7	1.294
	C_3 + SDS	-279.7	0.972
	N_3 + SDS	-249.7	4.44
	S_3 + SDS	-329.6	5.17
0.5 wt % Concentration	C_3	-505	12.77
	N_3	-245.1	2.3
	S_3	-505	1.58
	C_3 + SDS	-255.6	1.215
	N_3 + SDS	-216.2	1.215
	S_3 + SDS	-216.5	2.60
1 wt % Concentration	C_3	-545.1	2.64
	N_3	-245.1	2.3
	S_3	-355	2.02
	C_3 + SDS	-274.9	0.443
	N_3 + SDS	-189.9	0.803
	S_3 + SDS	-280	1.46

From the thermodynamic aspect bare Cu is nobler substrate compared to coated substrate because its corrosion resistance high. The current density (I_{corro}) of coated substrate has lower than bare Cu from table.1 & 2, so it can form protective graphene layer on Cu and can improve the corrosion resistance of substrate in chloride solution [27].

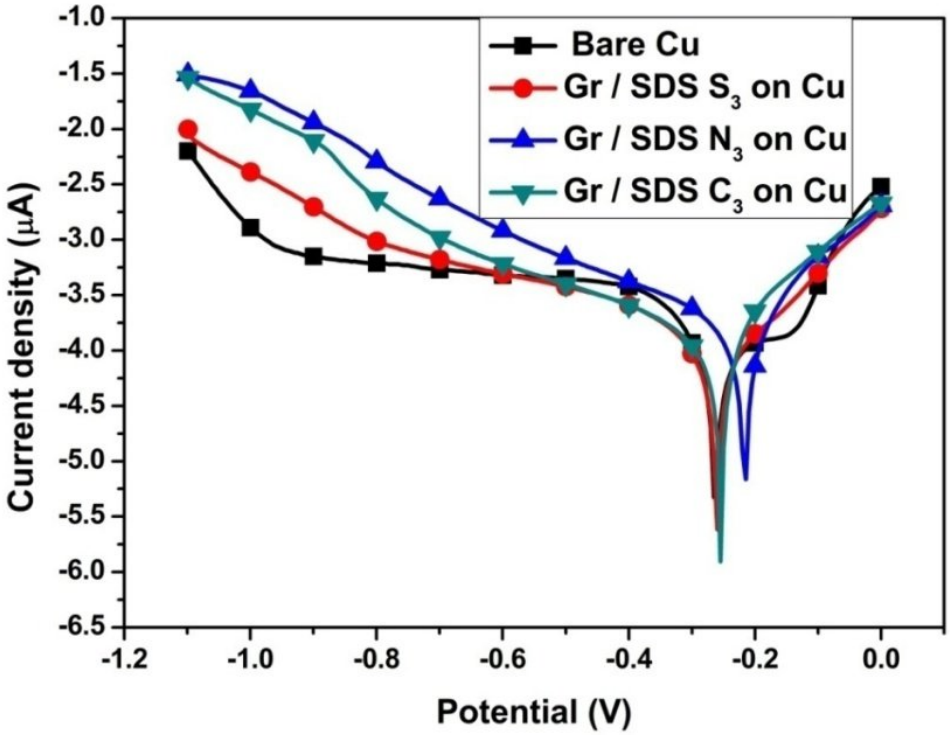

Figure 13: Potentiodynamic curves of bare Cu and 0.5 wt % concentration graphene with SDS coating on Cu

Form Table.1, the corrosion potential of 0.5 wt % concentration graphene with SDS coated on Cu has more positive values (-261.5mV, -216.2mV, -255.6mV) as compared to bare Cu (-264.1mV), means that the corrosion resistance of graphene SDS coated substrate high and it forms more corrosion protective layer. Without SDS coated substrate has more negative values and has not given effective protective layer because its corrosion resistance is very poor.

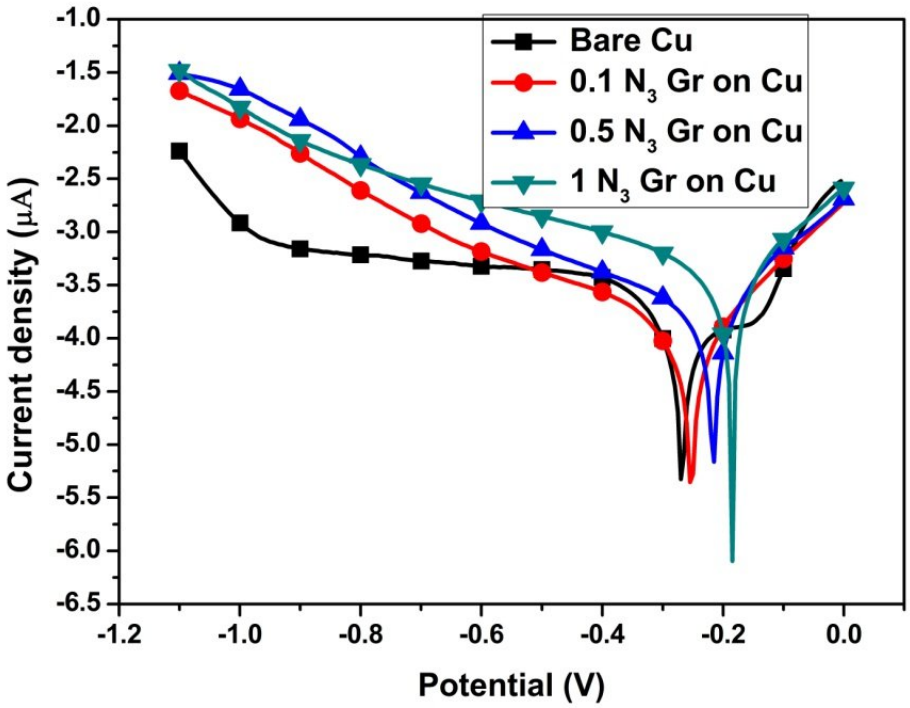

Figure 14: Potentiodynamic curve of bare Cu and nitric acid exfoliated graphene coating on Cu in various concentration

From Table 1, the nitric acid exfoliated graphene oxide deposited on Cu with and without SDS (N_3 and N_3+SDS) has more positive values compared to bare Cu (-264.1mV), which shows that nitric acid exfoliated graphene form corrosion protective layer on Cu substrate.

4.6 AFM analysis

Surface morphology of graphene deposited layer has further studied by topographical 3-D image using atomic force microscopy with surface scan area 20μm x 20 μm. Surface roughness of the EPD graphene thin layer was determined, which is listed in table 1 nitric acid exfoliated graphene nanosheets deposited on Cu in various concentration solution 0.1, 0.5, and 1 wt % respectively. 0.1 wt % graphene coated Cu has minimum roughness R_a = 0.39 μm corresponding to average height or thickness R_z = 0.63 μm, so that the smooth graphene layer forms on the Cu

surface compared to other. In lower concentration of EPD solution the thin layer formation take place is more uniform.

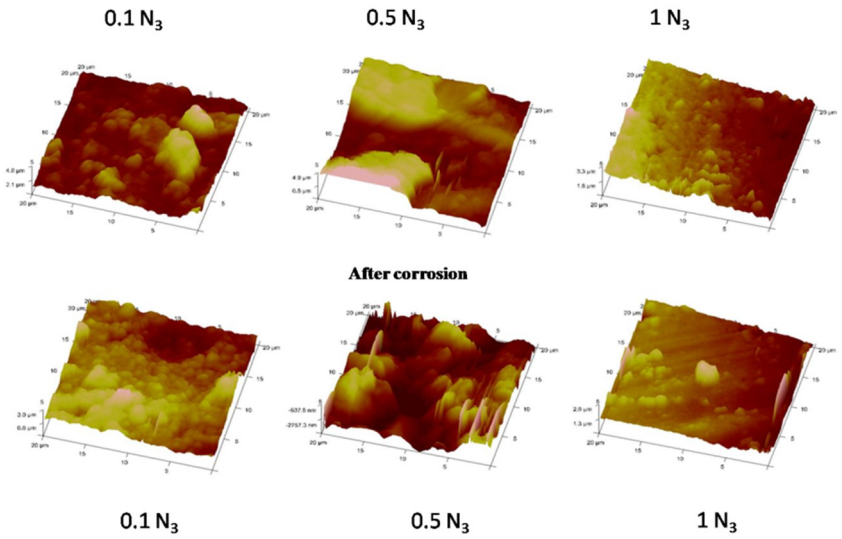

Figure 15: Topographical images of coated graphene on Cu in various concentration nitric GO solutions, (a) 0.1 (b) 0.5 & (c) 1 wt %

The surface roughness of EPD graphene layer on Cu is low as compared to corroded surface, which is show in table 2 because after corrosion oxide layer form on the surface.

Table 2: Roughness of EPD GO layer at different concentration before and after corrosion

Concentration	**Roughness (R_a) µm**	**After corrosion Roughness(R_a) µm**
0.1 wt % GO N_3	0.398	0.636
0.5 wt % GO N_3	0.906	1.23
1 wt % GO N_3	0.931	1.30

Chapter 05
Conclusions

5. Conclusions

In the present work has been studied the electrophoretic deposition of graphene on copper and its corrosion behavior. The results are abbreviated below:

- Graphene exfoliation in linear sweep voltametry has shows that exfoliation rate is high in 1.5M H_2SO_4 electrolyte and gives thin layer of graphene.

- XRD analysis has confirmed the d-spacing value of graphene nanosheets exfoliated in sulfuric electrolyte is high, hence the inter spacing layer of graphite sheet high during exfoliation.

- FESEM images of EPD of graphene oxide layer on Cu substrate have shows flakes and crust types microstructure and addition with SDS anionic surfactant were found densely packed and homogeneous structure.

- AFM has confirmed the roughness of graphene layer on Cu increasing with EPD concentration and after corrosion roughness also increased due to oxide layer on coating.

- Corrosion test has confirmed that the corrosion resistance properties are high in nitric GO solution and with SDS deposited on Cu.

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